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Oxygen potentials of plutonium and uranium mixed oxide

Masato Kato [a,*], Tetsuya Tamura [b], Kenji Konashi [c], Shigenori Aono [a]

[a] *Japan Nuclear Cycle Development Institute, Tokai Works, 4-33 Muramatu, Tokai-Mura, Ibaraki 319-1194, Japan*
[b] *Inspection Development Company, 4-33 Muramatu, Tokai-Mura, Ibaraki 319-1194, Japan*
[c] *Tohoku University, 2145-1313 Narita-chou, Oarai-chou, Ibaraki 311-1313, Japan*

Abstract

The oxygen potentials of $(Pu_{0.3}U_{0.7})O_{2-x}$ in the near stoichiometric region were measured by a thermogravimetric technique which was used to establish the equilibrium between the oxide phases and H_2/H_2O system gas. The experimental results of $(Pu_{0.3}U_{0.7})O_{2-x}$ show a consistent variation in P_{O_2} with O/M and temperature and are in agreement with other works. The relationship between the partial oxygen pressure and x in MO_{2-x} was evaluated by the lattice defect theory. The relationship in the hypo-stoichiometric region was $x \propto P_{O_2}^{-1/2}$ near the stoichiometric composition, and became $x \propto P_{O_2}^{-1/3}$ with a decrease in O/M.

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1. Introduction

The oxygen potential ($\Delta\overline{G}_{O_2}$) of mixed oxide (MOX) fuel is an important parameter to control irradiation behavior as well as the fabrication process [1,2]. The $\Delta\overline{G}_{O_2}$ is expressed as a function of the ratio of oxygen to metal (O/M). The stable structure of the MOX is fluorite in the range of the O/M ratio of 2 ± x [3,4]. In the range of near stoichiometric composition, the $\Delta\overline{G}_{O_2}$ changes drastically with the change of the O/M ratio. There are a number of experimental data of the $\Delta\overline{G}_{O_2}$ for UO_2 [5–11], which is the fuel in light water reactors (LWRs). On the other hand, data for MOX fuel which is used in fast reactors (FRs) [12–23] are limited. In this work, the $\Delta\overline{G}_{O_2}$ was measured for the MOX fuel with the composition of $(Pu_{0.3}U_{0.7})O_{2-x}$, which has been used as a core fuel of the FR 'Monju'.

Edwards et al. [15] measured the $\Delta\overline{G}_{O_2}$ of $(Pu_{0.23}U_{0.77})O_{2\pm x}$ by a thermogravimetric technique, where the equilibrium condition was established in the system of the oxide phases and CO/CO_2 gas phase. The $\Delta\overline{G}_{O_2}$ of the MOX with the content of 30% Pu was reported by Markin et al. [12,13]. They measured the $\Delta\overline{G}_{O_2}$ of $(Pu_{0.3}U_{0.7})O_{2\pm x}$ at temperatures from 800 °C to 1100 °C by the EMF method. Woodley [20] measured the $\Delta\overline{G}_{O_2}$ of $(Pu_{0.25}U_{0.75})O_{2\pm x}$, $(Pu_{0.4}U_{0.6})O_{2\pm x}$ and PuO_{2-x}, and evaluated the Pu content dependency on the $\Delta\overline{G}_{O_2}$ of the MOX. There is a difference between Woodley's data and Markin's data. In the present work, the $\Delta\overline{G}_{O_2}$ of $(Pu_{0.3}U_{0.7})O_{2-x}$ was measured by a thermogravimetric technique with an inert gas/H_2/H_2O gas mixture.

2. Experimental

2.1. Sample preparation

The starting materials were prepared by the microwave denitration method [24], in which the plutonium

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[*] Corresponding author. Tel.: +81 29 282 1111; fax: +81 29 282 9473.
E-mail address: kato@tokai.jnc.go.jp (M. Kato).

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to uranium ratio was controlled in the nitrate solution. The $(Pu_{0.3}U_{0.7})O_2$ powder was pressed and sintered (1700 °C for 3 h in $Ar/5\%H_2$ mixed gas) to make a pellet (diameter, 5.4 mm). A pellet was crushed using an agate mortar and pestle to obtain the sample for the measurement of $\Delta\overline{G}_{O_2}$. Part of a crushed pellet was annealed at 850 °C for 8 h in an atmosphere of $\Delta\overline{G}_{O_2}$ of −420 kJ/mol to adjust the O/M to 2.00 [12,13]. The weight of the sample was measured to be 199.995 mg. The impurities in the raw material were chemically analyzed and are listed in Table 1. The homogeneity of the sample was confirmed by X-ray diffraction and by electron probe micro analyzer.

2.2. Apparatus and experimental technique

The apparatus for measuring the $\Delta\overline{G}_{O_2}$is shown schematically in Fig. 1. Thermal gravimetry and differential thermal analysis (TG–DTA) were used to measure the $\Delta\overline{G}_{O_2}$. The TG–DTA measurements were made with a RIGAKU TG8120 model which was modified to be air tight. The device was put in a glove box isolated from vibration by four air dampers. The weight change of ±1 μg which corresponds to the O/M change of ±0.0001, could be measured by TG with a horizontal differential type balance. The O/M ratio was calculated from the weight change of the sample by

$$O/M = 2.0000 - 16.894 \cdot \Delta W/W, \tag{1}$$

where ΔW is the change of sample weight and W is the sample weight at O/M of 2.0000. Although there was a small drift in the weight measurement, it could be canceled completely by measurements of the sample weights before and after the experiment under the standard condition of $\Delta\overline{G}_{O_2}$.

Table 1
Typical impurities from raw material analysis

	ppm
Ag	4
Al	<50
B	<2
Ca	<50
Cd	<2
Cr	90
Cu	5
Fe	390
Mg	<20
Mn	10
Mo	<20
Na	260
Ni	40
Si	<20
V	<50
Zn	<50

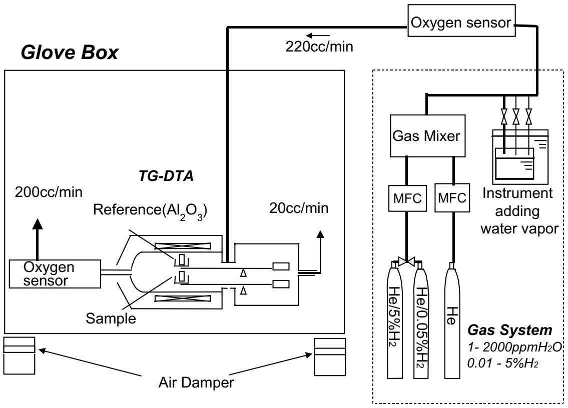

Fig. 1. Schematic drawing of the apparatus.

The $\Delta\overline{G}_{O_2}$ in the atmosphere inside the device was controlled by the H_2O/H_2 ratio, which was established by mixing inert gas (He or Ar) and inert gas containing 5% $H_2$and by adding water vapor. Considering the reaction of $H_2O \leftrightarrow H_2 + 1/2O_2$, the equilibrium of the H_2O/H_2 system is expressed by

$$\Delta G_f = -RT \ln \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{1/2}}, \tag{2}$$

where R is gas constant (8.3145 J/mol K), T is the absolute temperature (K) and P_i is partial pressure of i (atm). The free energy, ΔG_f, can be calculated by [25]

$$\Delta G_f = -246440 + 54.81 \cdot T. \tag{3}$$

The P_{O_2} of the off gas from the TG–DTA device was measured at 700 °C using stabilized zirconia oxygen sensors. The H_2O/H_2 ratio at 700 °C was calculated by Eq. (2). The P_{O_2} at the position of the sample was calculated under the assumption that the above ratio of H_2O/H_2 was the same as that at the sample position. The experimental error of the oxygen potential was estimated to be less than 1 kJ/mol based on the measurement of standard materials of Fe/FeO [25]. The P_{O_2} measurements were carried out at 1000 °C, 1200 °C, 1300 °C and 1350 °C in an atmosphere of $Ar/H_2/H_2O$ or $He/H_2/H_2O$ mixed gas.

3. Results and discussion

Fig. 2 shows the TG and the P_{O_2} curves for the measurement at 1300 °C. It is observed that the TG curve changes according to the change of P_{O_2} and reaches equilibrium with the P_{O_2} of the atmosphere in less than 15 min. A short time measurement by using a small sample could result in measuring a small variation in O/M ratio as shown in Fig. 2.

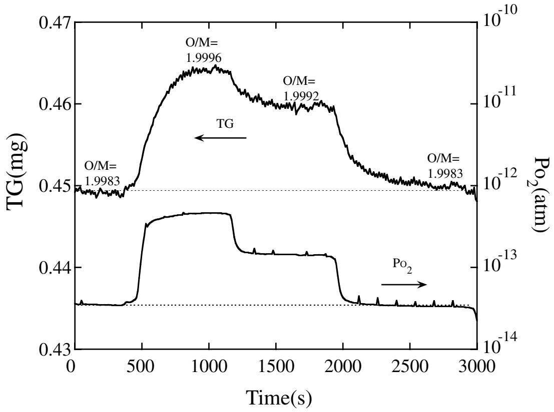

Fig. 2. The TG and the P_{O_2} curves measured at 1300 °C.

The P_{O_2} of $(Pu_{0.3}U_{0.7})O_{2-x}$ was measured at 1000 °C, 1200 °C, 1300 °C and 1350 °C. The oxygen potentials, $\Delta\overline{G}_{O_2}$, were calculated from the P_{O_2} by the following equation

$$\Delta\overline{G}_{O_2} = -RT\ln P_{O_2}. \tag{4}$$

Fig. 3 shows the $\Delta\overline{G}_{O_2}$ as a function of the O/M ratio. Systematic data with little ambiguity are obtained by using the sophisticated O/M measurement device. It can be said that the data are useful to understand the mechanism of the change of the $\Delta\overline{G}_{O_2}$ in the O/M-sensitive region in the neighborhood of stoichiometry. Markin's data [12,13] on $\Delta\overline{G}_{O_2}$ at 1100 °C $(Pu_{0.3}U_{0.7})O_{2-x}$ are also shown in Fig. 3 for comparison. The present data are in good agreement with Markin's data. The $\Delta\overline{G}_{O_2}$ can be expressed as a function of temperature by

$$\Delta\overline{G}_{O_2} = \Delta\overline{H}_{O_2} - T\cdot\Delta\overline{S}_{O_2}, \tag{5}$$

where $\Delta\overline{H}_{O_2}$ is partial molar enthalpy and $\Delta\overline{S}_{O_2}$ is partial molar entropy. Figs. 4 and 5 show $\Delta\overline{H}_{O_2}$ and the $\Delta\overline{S}_{O_2}$ calculated using the present experimental data,

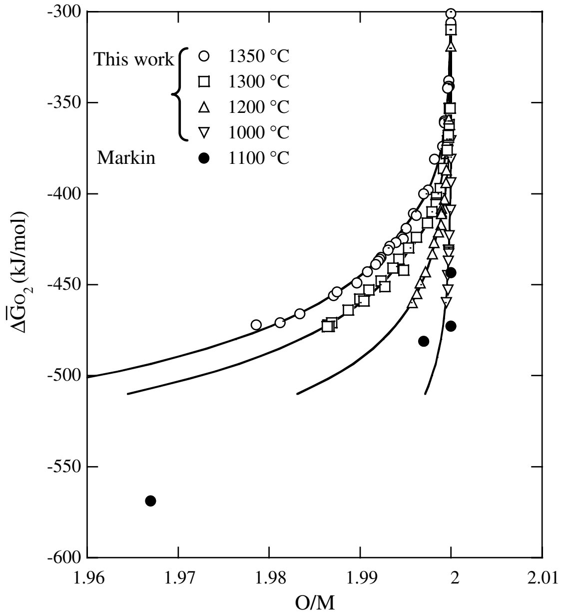

Fig. 3. Variation in the oxygen potential of $Pu_{0.3}U_{0.7}O_{2-x}$ with composition at temperatures from 1000 °C to 1350 °C.

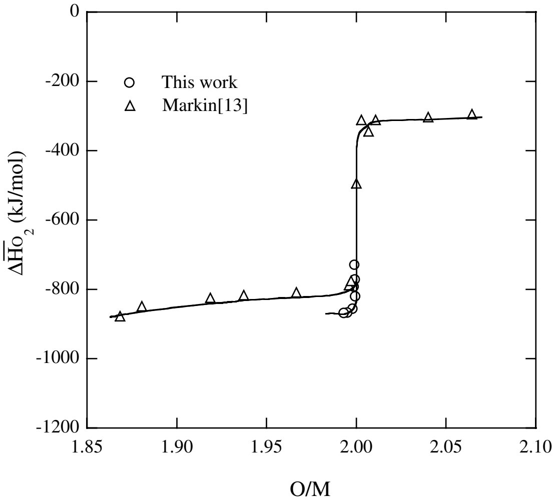

Fig. 4. $\Delta\overline{H}_{O_2}$ as a function of O/M ratio.

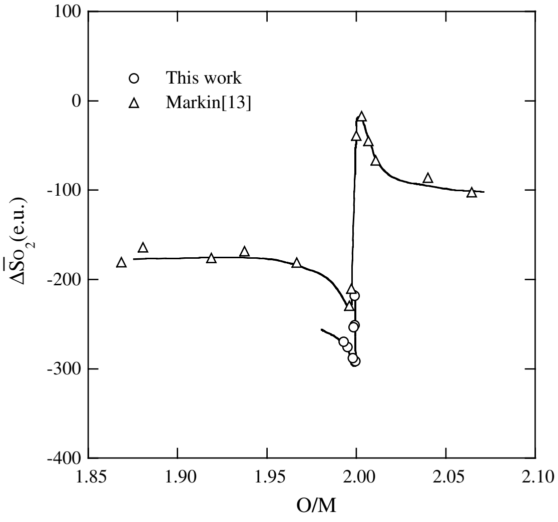

Fig. 5. $\Delta\overline{S}_{O_2}$ as a function of O/M ratio.

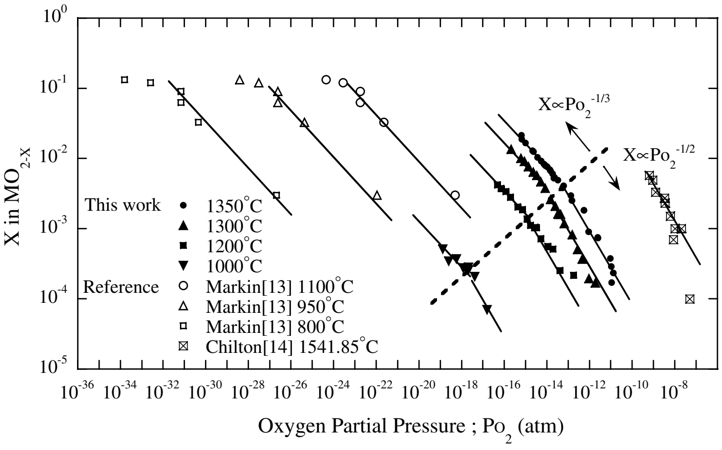

Fig. 6. Relationships between P_{O_2} and x in MO_{2-x}.

respectively. The present $\Delta\overline{H}_{O_2}$ and the $\Delta\overline{S}_{O_2}$ are somewhat lower than those of Markin's data [13] but the agreement in the dependencies of $\Delta\overline{H}_{O_2}$ and the $\Delta\overline{S}_{O_2}$ on O/M are quite good for both.

Many models have been studied to predict $\Delta\overline{G}_{O_2}$ as a function of temperature and composition [1,2,11,23,26]. Blackburn's group developed the oxygen potential model based on the chemical reaction between metal ions and oxygen [1,2]. Recently, Nagai [26] improved the Blackburn model so that it can reproduce experimental data of UO_{2+x}, MOX and PuO_{2-x}. More mechanistic models have been developed based on lattice defect theory [27–29]. The relationship between the P_{O_2} and x in MO_{2-x} is written by

$$x \propto P_{O_2}^{1/n},$$

where n is a characteristic number identifying the type of lattice defect.

The present data of P_{O_2} provide useful information to find the dependency of P_{O_2} on the composition parameter of x. Fig. 6 shows the relation between P_{O_2} and x in MO_{2-x}. Data of Markin and McIver [12] and of Chilton [14] are also shown there to indicate the relationship in the large x region. Markin and McIver [12] measured ΔG_{O2} of MOX at 800 °C, 950 °C and 1100 °C by a galvanic cell method, while Chilton [14] measured the $\Delta\overline{G}_{O_2}$ of $(Pu_{0.31}U_{0.69})O_{2-x}$ at 1541.98 °C by a thermogravimetric method using CO/CO_2 mixed gas. The experimental results of $(Pu_{0.3}U_{0.7})O_{2-x}$ show that there is a consistent variation in P_{O_2} with O/M and the temperature, agreeing with other works [12–14]. The relationship in the hypostoichiometric region is $n = -2$ near stoichiometric composition, and the value of n changes to $n = -3$ in both the present and the other data with a decrease in O/M. The boundary between two areas with $x \propto P_{O_2}^{-1/3}$ and $x \propto P_{O_2}^{-1/2}$ is shown with a dotted line in Fig. 6. The area with $x \propto P_{O_2}^{-1/2}$ is extended with increasing temperature.

4. Conclusion

The oxygen potentials of $(Pu_{0.3}U_{0.7})O_{2-x}$ were measured by a thermogravimetric technique. The measurements have been done in a region of near stoichiometric composition at temperatures from 1000 °C to 1350 °C, where $\Delta\overline{G}_{O_2}$ changed sensitively in response to O/M. Systematic data have been obtained with little ambiguity. The present data were in good agreement with Markin's data.

The relationship between the partial oxygen pressure (P_{O_2}) and x in MO_{2-x} was analyzed based on lattice defect theory. The relation of $x \propto P_{O_2}^{-1/2}$ was found in the region of near stoichiometric composition.

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